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THE CHEMISTRY WHICH CREATED GREEN RIVER FORMATION OIL SHALE

By

J. W. Smith
Consultant, 1472 North Fifth Street, Laramie, Wyoming 82070

INTRODUCTION

The Green River Formation oil shales have been the object of only a limited amount of effort aimed at describing how they came to be. Much that has appeared looks at only one facet of a complex, integrated system. In 1925 Bradley (2) published an initial postulate which still has much strength although Bradley ultimately was moved away from this idea. Smith and Robb (16), Smith (13), and Smith and Lee (15) have extended Bradley's postulate to develop a comprehensive picture of the genesis of the Green River Formation deposits. These are summarized here.

GREEN RIVER FORMATION CHARACTERISTICS

The Eocene Green River Formation is unique in organic-rich sedimentary deposits. Nothing like it exists elsewhere. Although many collections of sedimentary rocks containing organic matter exist, the Green River Formation contains spectacularly large amounts making up much larger than average volume fractions of the total sediment. In addition this deposition persisted through literally millions of years. An excellent example of this is the oil shale sampled by the U. S. B. M. -A. E. C. Colorado Corehole No. 1 which demonstrated the existence of about 2100 feet (640 meters) of continuous oil shale (17). Average organic content through this section is nearly 25 volume percent of the total rock. This organic matter is remarkably uniform and relatively rich in hydrogen. The carbon-to-hydrogen weight ratio in organic matter throughout the Formation is about 7.7-7.8, similar to the high end of the petroleum spectrum and much lower than most other oil shales of the world. The only change in the nature of the organic matter through the 2100-foot section is decarboxylation with depth of burial (12,14). A study purporting to detect variations in organic matter through the oil shales in Colorado Corehole No. 1 (10) actually demonstrates the remarkable and persistent similarity of the organic matter in the Green River Formation thickness deposited over millions of years.

The lateral consistency of the Green River Formation deposition is also remarkable. Figure 1 compares oil yield histograms for about 500 feet (150 meters) of continuous oil shale at two locations in the Green River Formation (19). Figure 2 shows the locations of these two coreholes--about 85 miles apart. These histograms are deposition profiles correlated in time. They demonstrate the gross lateral persistence of oil shale deposition. This is also demonstratable on a much smaller scale. Figure 3 shows the stratigraphic variation across a 2-inch (5 cm) block. Trudell et al. (18) published a classic photograph indicating comparability of such markings over a 75-mile (120 km) span. A third level of persistence exists on a microscale. Annual depositional cycles produced varying. The varves are too small ($\sim 30\mu$) to be photographed and reproduced here, but they couldn't even be located if they were not laterally persistent.

Associated with the lateral continuity of the formation is the lateral consistency of mineral composition. This might be startling except for the fact that the mineral suite in Green River Formation oil shale is uniform stratigraphically as well as laterally. This mineral suite is authigenic, formed by the chemistry of the lake. Two major mineral variations warrant mention, because they appear to belie mineral uniformity. One is the illite concentration deposited early in the formation's sedimentary history which was rather abruptly replaced by dolomite. The other is the appearance of truly remarkable minerals--nahcolite (NaHCO_3), dawsonite [$\text{NaAl}(\text{OH})_2\text{CO}_3$], shortite ($\text{Na}_2\text{CO}_3 \cdot 2\text{CaCO}_3$), and trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$). These minerals are rare in the rest of the world but appear in billions of tons in the Green River Formation. An additional peculiarity is the formation of shortite and trona in the Wyoming deposits and the development of dawsonite and nahcolite in Colorado.

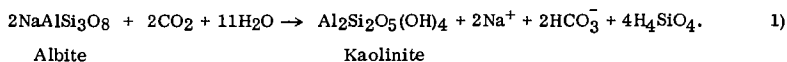
These characteristics pose a set of rather difficult problems in describing the genesis of the Formation. A geochemical postulate has been developed (15) to explain this genesis and its peculiarities. This pattern is outlined.

LAKE UINTA'S POSTULATED CHEMICAL HISTORY

Depositional conditions postulated for the Green River Formation must accommodate the major requirements described above. Colorado's deposits, formed in ancient Lake Uinta, offer the most complete example. Generalizations must be made in trying to evaluate briefly the conditions which formed Green River oil shale through perhaps six million years. Because the oil shale is virtually continuous, the conditions were also continuous. Consequently, generalization is appropriate.

The basic postulate for oil-shale genesis is a stratified lake, separating the lake waters into two non-mixing layers. Bradley (2) recognized this requirement in his early studies of the Green River Formation. A number of permanently stratified lakes, called meromictic lakes, exist currently in the United States (3) and several sets of conditions leading to stable stratification have been outlined by Hutchinson (6). Colorado's Lake Uinta probably began in the northwestern part of the present Piceance Creek Basin, where a long sequence of normal lacustrine sediment occurs. Thermal density differences probably produced the initial stratification. Three primordial lakes probably existed--the one in Colorado's Piceance Creek Basin, one in Wyoming north of the Uinta Mountains and one in Utah south of the Uinta Mountains. Since all three lakes did the same thing, the Green River Formation's development may have been due to minerals arising from the Uinta Mountains.

Hydrolysis of local silicates and aluminosilicates in the stratified lake's lower layer began to build up a chemical stratification. Garrels and Mackenzie (5, p. 175) give the following equation as an example of this hydrolysis, using albite as a simple specimen:



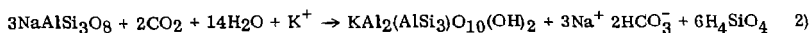
Notice that acid, represented here by CO_2 and water, is consumed and that sodium and bicarbonate ions are produced as albite alters to kaolinite. Decomposition of organic matter furnished carbon dioxide. Concentration of sodium carbonates and other dissolved salts in solution in water of the stratified lake's lower layer built up, raising the water density. The evolution from normal lacustrine sediments to oil shale in the northwestern part of the Piceance Creek Basin is continuous and without evidence of evaporative cycles (18). The acid-consuming hydrolysis indicated in Equation 1 probably was the primary mechanism which built up the water density. This created a remarkably stable chemical stratification in ancient Lake Uinta, lasting through the entire period of oil-shale deposition.

Permanent stratification of ancient Lake Uinta was accompanied by a limitation of the supply of materials reaching the lake's lower layer. Currents in the water of the lower layer had to be very slow or the organic matter deposited uniformly in the tiny varves would have accumulated unevenly. Currents in the water of the upper layer could not be strong because of the relatively small flow of water through a huge area. In slow currents larger clastic materials deposit near the lake shore. Only air-borne particles and water-borne particles small enough to remain suspended in slow currents could be distributed over the lake's huge area. Tiny particles, predominantly silicates, and organic debris plus the small amount of clastic material deposited on the edges of the lake made up the supply of material available to the lake. Both the amount and the composition of this supply was limited and continued to be so through much of the time oil shale was deposited.

Organic debris from the lake's upper layer fell into the lower layers. This organic matter made up a relatively large portion of the material reaching the lower layer of the stratified lake, not because the lake producing it teemed with life (it didn't) but because the lake strongly limited the available mineral matter. The organic matter chemically consumed the available oxygen. In the stratified lake no oxygen supply could reach the bottom layer which quickly became, and remained, a reducing environment. The reducing environment became powerful enough to continually hydrogenate organic matter, making the organic residue rich in hydrogen and poor in oxygen. Oil-shale deposition began.

Water of the lower layer must have been lethal to macrolife and probably also to microscopic life--bioturbation would have destroyed the varves and lamina. The upper or surface layer, however, must have been fresh enough for life to exist because organic matter was continuously deposited in the sediment. In its travel through the lake's lower layer, the organic matter was exposed to basic reducing solutions which digested it and homogenized it. Only particular chemical structures would survive exposure to the basic environment, automatically selecting similar materials. In addition, the strongly reducing environment in the lake and the sediment would hydrogenate the organic matter to produce the hydrogen-rich organic matter. This mode of deposition over a wide area explains the lateral uniformity observed in element composition of organic matter in Mahogany zone oil shale (11), and the similarity in properties of the oil-shale organic matter over the entire deposit. The paucity of microfossils in the oil shale, limited largely to an occasional gas scale and the like, illustrates the power of the lake's lower layer to digest organic matter.

As hydrolysis of the silicates and aluminosilicates continued (Equation 1), dissolved sodium and bicarbonate ions were continually produced, and acid was consumed. The pH of the water gradually increased. Formation of kaolinite was replaced by formation of montmorillonite and finally by production of illite. The reactions indicated by Equation 1 were replaced by the family of reactions indicated in Equation 2, written using the hydrolysis of albite as an example.



Albite

Illite

Loughnan (7) gives the above chemical composition for illite, pointing out that illite is characterized by substitutions in the silica sheet. As pH of the lake water increased, silica became more mobile than alumina. Formation of the relatively silica-poor illite resulted. Dehydration of the dissolved silica in the sediment's water (Equation 3) produced quartz. The large amounts of illite from the reactions represented by Equation 2 and the quartz from Equation 3 formed the major mineral constituents in the oil shales below the mineral change.



Quartz

The illite-producing reaction in Equation 2 continued to consume acid, apparently in amounts greater than could be supplied by CO_2 from the organic matter. This made the water of the lower layer progressively more basic. When the pH of this water exceeded 10, alumina also became mobile. Solubility of both SiO_2 and Al_2O_3 increases dramatically as the solution pH increases past 10. The water of the lower layer was now primarily a sodium carbonate solution, strongly basic and strongly reducing. The protective layer of $\text{Al}(\text{OH})_3$ which had continually formed around aluminosilicate particles now dissolved because of the amphoteric behavior of aluminum. Consequently, when the tiny clastic particles entered this water, they were destroyed, and the aluminate ion also began to accumulate in the lake's lower layer. Illite was no longer produced in quantity from the protected skeletons, and the mineralogy of the resulting oil shales changed abruptly.

The organic matter being deposited changed little across this major change in minerals, but the organic matter now became a major factor in the production of oil-shale minerals. As organic matter, produced seasonally in the lake's upper layer, collected on the lake bottom, it trapped water from the lake's lower layer. This water had a pH on the order of 11, was strongly reducing, and had continued to build up a supply of dissolved materials. Laboratory tests have shown that organic matter from the Green River oil shales has a large capacity for forming a water-retaining suspension (16). In addition, the sediment probably acted as an ionic filter, retaining ions as water was forced from the sediment. Reductive conditions in the sediment continued to operate on the organic matter which evolved CO_2 and some H_2S . These gases dissolved in the interstitial water, lowering its pH.

The limits of reduction potential and pH in the sediments which became oil shale of the Parachute Creek Member can now be defined. These are presented as the shaded area in Figure 4. The block's bottom boundary (4) represents the lower stability limit of water. At reductive potentials below this line, water breaks down to yield hydrogen, illustrating the strength of the hydrogenating environment in the sediment. The upper boundary, defined by the ratio of sulfate to sulfide ion, is drawn three orders of magnitude below the Eh values represented by equal parts of sulfate and sulfide ions because sulfate has not been observed in unweathered Parachute Creek sediments. The lower pH boundary is set because of strong bicarbonate (nahcolite) buffering at about pH 8.4. The upper boundary is set at a pH of 10 because of the sharp increase in silica and alumina solubility above this pH. The pH of the interstitial water probably averaged about 9.

With the sharp lowering of pH from perhaps 11 to 9 at the organic sediment interface, silicates began to form from the interstitial water trapped in the sediment. The solubility of both silica and alumina decreases sharply as pH changes from 11 down to 9. The resulting chemical conditions in the sediment encouraged development of authigenic feldspars and formation of quartz. Silicate precipitation should be enhanced by large amounts of organic matter producing larger amounts of CO_2 . Silicate formation definitely increases with increasing organic matter in Colorado's Green River oil shales (9). Silicates generated in this manner should tend to concentrate in the organic layers and in the organic-rich (dark) fraction of the light-dark varve cycle.

Smith and Robb (16) describe the authigenic formation of dolomite, calcite, and aragonite in Lake Uinta. Calcite was formed in the lake's lower layer from the calcium released by chemical digestion of silicate and aluminosilicates. Calcium was released to a calcite-saturated sodium carbonate solution, immediately forming calcite. The calcite crystals settled to the lake bottom as a continuous and very dispersed shower of tiny calcite particles. The Mg^{++} and Fe^{++} released by dissolving particles precipitated as $\text{Mg}(\text{OH})_2$ and $\text{Fe}(\text{OH})_2$, also descending to the lake bottom.

When these hydroxides were enclosed in the sediment they dissolved, releasing Mg^{++} and Fe^{++} to form the Green River Formation's iron-bearing dolomite. Part of the iron was used to form pyrite. During deposition of the Mahogany zone, aragonite formed seasonally in the lake's upper layer, fell to the lake bottom, and was partially dolomitized and partially preserved (16). This generated the dolomite-rich light layers in Mahogany zone varves. Thus the chemical conditions in the stratified lake Uinta explain the lateral persistence of the tiny varves and the large laminations, which can be correlated over huge areas, reflecting area wide changes particularly in the growing conditions that produced the depositing organic matter.

One event in the life of Lake Uinta remains to be explained, the production of the unique saline mineral suite. The saline mineral suite consists of dawsonite [$NaAl(OH)_3CO_3$] with its accompanying nordstrandite [$Al(OH)_3$], nahcolite ($NaHCO_3$), and halite ($NaCl$), deposited in the Parachute Creek Member around the early depositional center. Two factors combined to produce the saline minerals: 1) the continual buildup of sodium carbonate and aluminate ion in the water of the lake's lower layer, and 2) the gradual loss of water from the lake's lower layer and the accompanying increase in concentration of the materials in solution. The hydrolysis mechanism continuously supplying sodium carbonate and aluminate ion to this water has been described (see Equation 2). The loss of water from the lake's lower layer had to be a mechanism at the lake's edges because the upper layer of Lake Uinta continued to supply organic matter to the lake bottom through the deposition of the saline minerals.

Dawsonite occurs in oil shale as a matrix mineral formed from the lake water as a precipitate in the sediment. Bader and Esch (1) synthesized dawsonite by bubbling CO_2 into a sodium aluminate solution at a pH of 11. As the pH of their solution dropped, dawsonite precipitated. Dawsonite was obtained only when the sodium carbonate to aluminate ratios were higher than 15 to 1. This synthesis method is almost an exact description of the natural mechanism which formed dawsonite in the sediment. Carbon dioxide from the deposited organic matter performed on the sodium carbonate and aluminate ion dissolved in the trapped water exactly as in the synthesis method, forming dawsonite.

Nahcolite crystallization was also produced by CO_2 from organic matter. Sodium carbonate in the interstitial water was converted to sodium bicarbonate by the reaction shown in Equation 4.



By this reaction 106 grams of sodium carbonate becomes 168 grams of sodium bicarbonate. Sodium bicarbonate is less soluble than sodium carbonate by a factor of 3 or 4. As the concentration of the salts that were dissolved in the lower layer gradually increased, a point was reached where nahcolite ($NaHCO_3$) began to crystallize in the sediment. These crystals grew as the sodium bicarbonate dissolved in the interstitial water migrated to them. Crystals that grew in sediment make up most of the nahcolite occurrence in the Piceance Creek Basin. As Milton and Eugster (8) point out, nahcolite is the solid phase expected at the relatively high CO_2 pressure in the unconsolidated sediment. None of the other sodium carbonate crystal forms known to occur in nature have been found in core from the Piceance Creek Basin. In Colorado the stratified lake persisted through saline mineral deposition. In Wyoming, however, the corresponding lake went nearly or completely to dryness, losing its protective top. When exposed to atmospheric levels of CO_2 , sodium carbonate solutions crystallize trona. Wyoming's lake did.

Smith and Lee (15) tested stability of the postulated chemical stratification. These tests indicated that the density stratification would persist largely unmixed through all possible stresses--earthquakes, seiches, tides, temperature variations, and even windstorms stronger than any known.

SUMMARY

The genesis pattern presented for Green River Formation oil shale explains the major observation. Deposition of relatively large quantities of hydrogen-rich organic matter in the oil shales is a natural consequence of the chemical conditions (basic water and reducing atmosphere) and the physical limitation of clastic materials developed in the stratified ancient Lake Uinta. Stability of the stratification produced the continuous deposition of the organic matter and its uniformity over the deposit. Authigenic formation of the oil-shale minerals proceeds naturally from the lake stratification, and the varve production stems from the seasonable development of organic matter. The lake's stratification produced uniform deposition over the entire area it covered, making the correlatable lateral persistence of the thin laminations a natural consequence. As the lake developed, the attack on aluminosilicates by sodium carbonate in the lake's lower layer produced a silicate skeleton protected by aluminum trihydroxide. On deposition, this aluminum-rich skeleton formed illite in quantity. As the lake became more basic, the protecting aluminum hydroxide coating dissolved amphotERICALLY and illite production dropped at a specific point. Continual build-up of sodium carbonate and aluminate ion in the water of the lake's lower layer reached conditions which

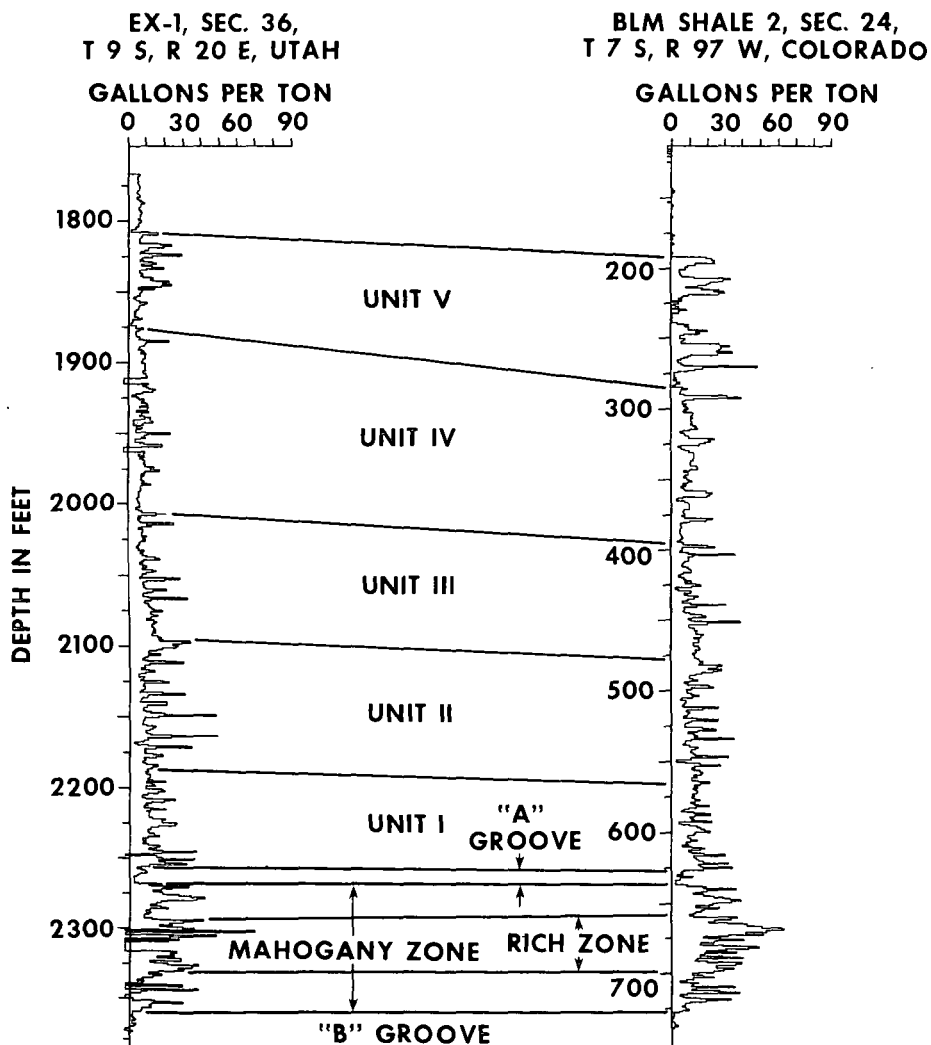


Figure 1. Oil Shale Correlations between Colorado and Utah Deposits.

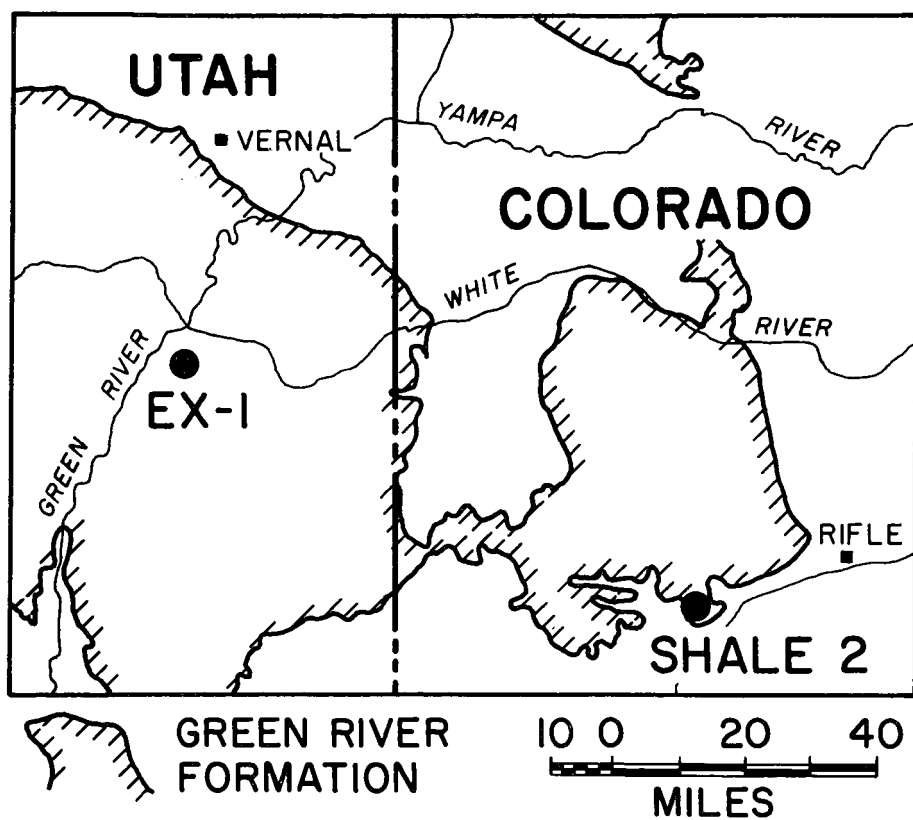


Figure 2. Oil Shale Locations compared in Figure 1.

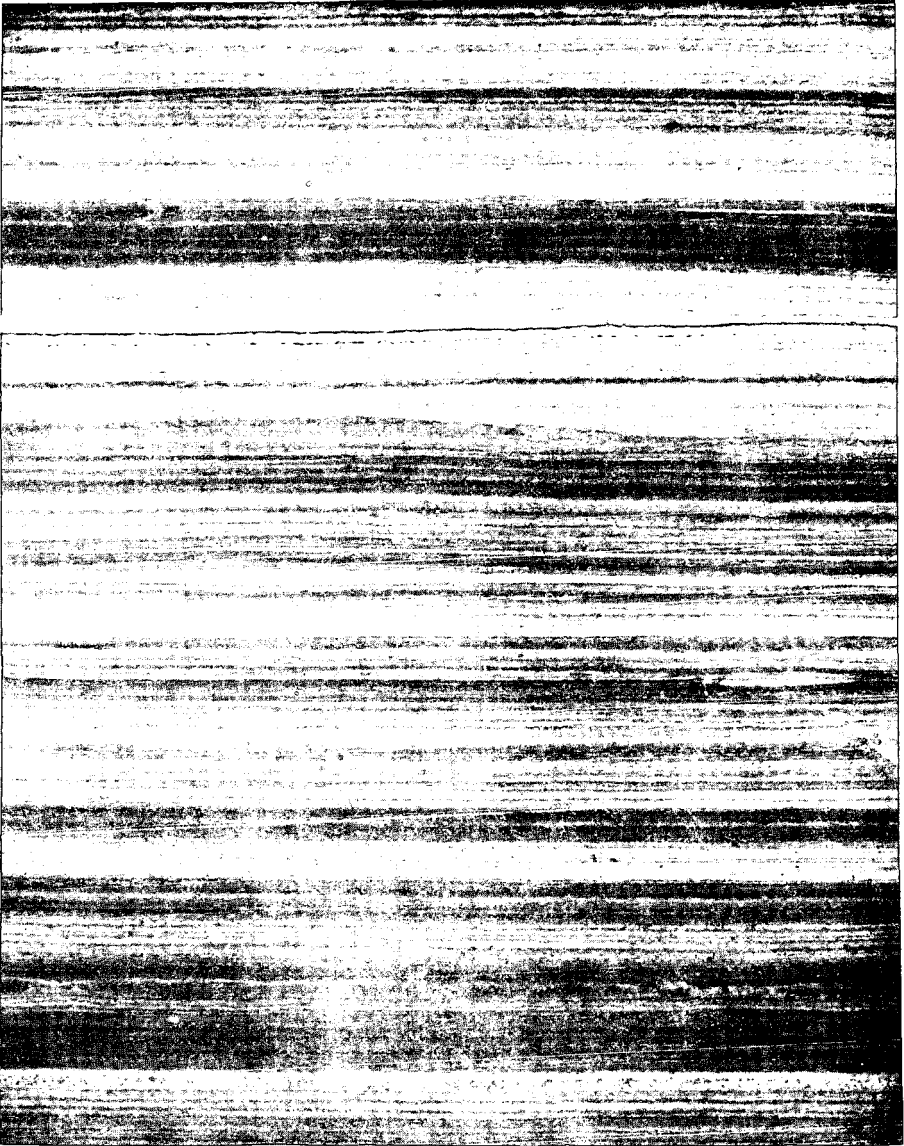


Figure 3. Oil Shale Laminations in a Two-Inch Block.

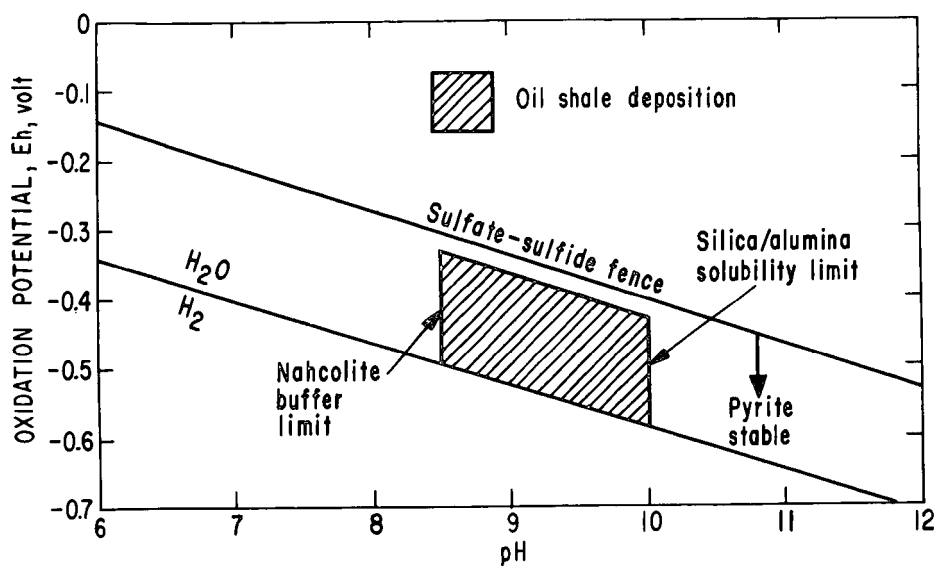


FIGURE 4 -Eh-pH limits in sediments which became Green River oil shale.

precipitated dawsonite and crystallized nahcolite in the sediment as a result of CO₂ production from organic matter.

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